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SYNTHESIS OF NEW LOW TEMPERATURE  
PETROLEUM-RESISTANT ELASTOMERS

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13. ABSTRACT <p>Three petroleum-resistant elastomers which are suitable for low temperature use have been prepared in approximately two pound quantities. The <math>[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n</math> copolymer has a <math>T_g</math> of <math>-77^\circ C</math>, is very inert chemically, and is soluble only in selected fluorocarbon solvents. The material does not burn in air in a direct flame. The copolymers, <math>[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n</math> and <math>[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n</math> are highly elastic and are unaffected by hydrocarbons and benzene, but are soluble in many polar organic solvents. Values for <math>T_g</math> of <math>-67^\circ C</math> and <math>-64^\circ C</math> have been obtained for these copolymers, respectively. Preliminary compounding studies of these three elastomers gave specimens with tensile strengths of 1080-1490 p.s.i. and elongations of 280-150%.</p> <p>Several process studies are described. The effect of cyclics on the course of derivatization was studied, but the results were inconclusive. The pH during hydrolysis appears to affect the molecular weight of the product. The removal of salts from the derivatized copolymer by several different methods was investigated.</p> <p>Exploratory synthesis to prepare polymers which contained the <math>(CF_3)_2CHO</math> moiety were largely unsuccessful. The <math>[(HCF_2C_3F_6CH_2O)_2PN]_n</math> homopolymer and a <math>[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n</math> copolymer with a substituent ratio of 1:8.4 were prepared.</p>			

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**SYNTHESIS OF NEW LOW TEMPERATURE PETROLEUM-RESISTANT ELASTOMERS**

Technical Report by  
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III

### ABSTRACT

Three petroleum resistant elastomers which are suitable for low temperature use have been prepared in approximately two pound quantities. These materials are:  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ ,  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$ , and  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$ .

The  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymer has a glass transition temperature of  $-77^\circ C$  and an initial decomposition point of  $300^\circ C$  in air (TGA,  $2-1/2^\circ$ /minute). The copolymer is very inert chemically and is soluble only in selected fluoro-carbon solvents. The material does not burn in air even in a direct flame. Samples were cured to give tensile strengths of 1100 p.s.i. and elongations of 280%.

The  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  elastomer has a glass transition temperature of  $-67^\circ C$  and an initial decomposition point of  $325^\circ C$ . The copolymer does not burn and is insoluble in benzene and the ASTM fuels, but is soluble in selected oxygenated solvents. Cured samples showed tensile strengths of 1080 p.s.i. and elongations of 200%.

The  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$  copolymer has a  $T_g$  of  $-64^\circ C$ . It is similar to the  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  copolymer in flammability and solvent and chemical resistance. Compounded samples had values of 1490 p.s.i. and 150% for tensile strength and elongation, respectively.

Several process studies are described. The effect of cyclics on the course of derivatization was studied, but the results were inconclusive. The pH during hydrolysis appears to affect the molecular weight of the product. The removal of salts from the derivatized copolymer by several different methods was investigated.

Exploratory synthesis to prepare polymers which contained the  $(CF_3)_2CHO$  moiety were largely unsuccessful. The  $[(HCF_2C_3F_6CH_2O)_2PN]_n$  homopolymer and a  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymer with a substituent ratio of 1:6.4 were prepared.

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## SYNTHESIS OF NEW LOW TEMPERATURE PETROLEUM-RESISTANT ELASTOMERS

### 1.0 INTRODUCTION AND SUMMARY

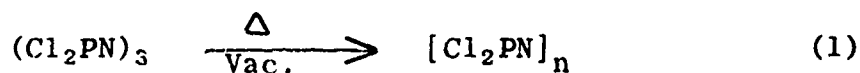
The development of the poly(fluoroalkoxyphosphazenes) has been sponsored in part by the Army Materials and Mechanics Research Center since February 1968. During the first year considerable progress was made towards the development of high strength chemically resistant elastomers which were useful over a wide temperature range (Ref. 1)(Ref. 2).

In the following year the preparation of half pound quantities of  $[(CF_3CH_2O)_2PN-(C_2F_7CH_2O)_2PN]_n$  and its precursor,  $[Cl_2PN]_n$ , was accomplished (Ref. 3). At the same time two new elastomers  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  and  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$ , which had good fuel resistance and low temperature properties were developed.

Last year, these three elastomers were further studied and scale-up to multipound quantities was demonstrated (Ref. 4). Process studies of the polymerization and derivatization were begun. The exploratory synthesis of new materials was continued.

The current contract, DAAG 46-71-C-0103 (March 4, 1971 - March 3, 1972), has the following objectives: (1) continue the development of promising poly(fluoroalkoxyphosphazenes) for utilization as Arctic rubbers, (2) optimize polymer properties and yields and determine reproducibility, and (3) develop appropriate cures and mechanical properties for the copolymers.

The synthetic route to poly(fluoroalkoxyphosphazenes) has been via the preparation of the soluble poly(dichlorophosphazene) precursor and subsequent reaction to form the completely substituted product.



When a mixture of two fluoroalkoxides is employed, copolymers are obtained which are either elastic or plastic dependent on the choice of substituents.

The  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymer has a glass transition temperature (DTA) of  $-77^\circ C$  ( $-107^\circ F$ ) and has an initial decomposition point of  $300^\circ C$  ( $572^\circ F$ ) in air on a thermobalance at a heating rate of  $2-1/2^\circ$ /minute. Intrinsic viscosities in  $F[CF(CF_3)CF_2O]_2CHFCF_3$  range as high as 2.4 dl./g. at  $30^\circ C$ . The copolymer appears unaffected by prolonged immersion in boiling water, common organic solvents, concentrated mineral acids, and concentrated potassium hydroxide, as well as by organic bases such as pyridine and formamide. It is soluble in the azeotrope of trichlorotrifluoroethane and acetone. When placed in a direct flame, the material softens and vaporizes but will not burn. Compounded samples have shown tensile strengths of 1100 p.s.i. and elongations of 280%.

The  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  copolymer has a  $T_g$  of  $-67^\circ C$  (DTA) and an initial decomposition point of about  $325^\circ C$  in air (TGA). This copolymer is unaffected by benzene, hydrocarbons and ASTM fuels. The elastomer is soluble in acetone, ethanol and the azeotrope of  $CCl_2FCClF_2$  with acetone. It has been obtained with an intrinsic viscosity as high as 5.5 dl./g. at  $28^\circ C$  in acetone. The copolymer will not burn when exposed to a direct flame. Preliminary compounding studies have given samples with a tensile strength of 1080 p.s.i. and an elongation of 200%.

The  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$  copolymer has a  $T_g$  of  $-64^\circ C$  (DTA). It has an initial decomposition point, chemical and solvent resistance and flammability which are similar to the  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  copolymer. Preliminary compounding with this copolymer has given samples with 1490 p.s.i. tensile strength and 150% elongation.

The three, low temperature, fuel-resistant elastomers described above have been prepared in approximately two pound quantities during this program. Little change in established procedure was required in these preparations. However, the purification of large quantities of these copolymers in solution was quite tedious and alternate methods were examined on a smaller scale.

Several process studies were undertaken. The intrinsic viscosities of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymers were found to be affected dramatically by pH during hydrolysis of the reaction mixture. This phenomenon remains under study.

Removal of salts from the derivatized copolymers without the use of solution extraction of salts and oligomers was attempted. The use of high speed agitation with swollen polymer appears promising.

The effect of relative reactivities of poly(dichlorophosphazene) and cyclic phosphazenes with sodium trifluoroethoxide and sodium heptafluorobutoxide was investigated. Little pattern was evident and some further work is indicated.

Once the successful preparation of the sodium salt of hexafluoroisopropanol was accomplished, the synthesis of several polymers which contained that moiety was attempted. The polymers attempted were:  $[\{(\text{CF}_3)_2\text{CHO}\}_2\text{PN}]_n$ ,  $[\{(\text{CF}_3)_2\text{CHO}\}_2\text{PN}-(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}]_n$ ,  $[\{(\text{CF}_3)_2\text{CHO}\}_2\text{PN}-(\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O})_2\text{PN}]_n$ , and  $[\{(\text{CF}_3)_2\text{CHO}\}_2\text{PN}-(\text{HCF}_2\text{C}_5\text{F}_{10}\text{CH}_2\text{O})_2\text{PN}]_n$ . These materials either contained unreacted chlorine or were too insoluble for study.

The preparation and characterization of new poly(fluoroalkoxyphosphazenes) was continued. The  $[(\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O})_2\text{PN}]_n$  homopolymer and a  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$  copolymer with a substituent ratio of about 1:6 were prepared.

## 2.0 LARGE SCALE PREPARATION OF LOW TEMPERATURE PETROLEUM-RESISTANT COPOLYMERS

### 2.1 Preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$

The procedures for preparation and purification of this copolymer have been reported previously (Ref. 4). Distilled hexachlorophosphazene (1350 g.) was polymerized at 270°C for 89 hours and at 250°C for 35 hours. The  $[Cl_2PN]_n$  polymer (1200 g., 89% conversion) was divided and a portion (600 g., 5.2 moles) in 2 liters of dry benzene was used for the preparation of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ . Trifluoroethanol (623 g., 6.2 moles),  $C_3F_7CH_2OH$  (1245 g., 6.2 moles), sodium (261 g., 11.4 moles) and 4.8 liters of tetrahydrofuran were used for the alkoxide preparation. The addition was conducted at reflux and reflux was continued overnight. Approximately 435 g. of oil were recovered after the reaction solvents were decanted and evaporated. Solids were placed in the azeotrope of  $CCl_2FCClF_2$  and acetone, treated with water, and benzene was added to cause precipitation of the copolymer (1058 g.). An additional 90 g. of oil were recovered from these solvents. Characterization of the copolymer is given in Table I.

### 2.2 Preparation of $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$

Distilled hexachlorophosphazene (966 g.) was polymerized for 24 hours at 270°C and 148 hours at 250°C. The  $[Cl_2PN]_n$  polymer (715 g., 74% conversion) was divided and a portion of the polymer (450 g., 3.9 moles) was dissolved in three liters of dry benzene. The fluoroalkoxides were prepared at 40°C in dry tetrahydrofuran from sodium (187 g., 8.2 moles),  $CF_3CH_2OH$  (448 g., 4.5 moles), and  $HCF_2C_3F_6CH_2OH$  (1040 g., 4.5 moles). The mixture was stirred overnight at 40°C to complete the reaction and the solution had a slight brown color. The  $[Cl_2PN]_n$  polymer solution was added in five hours to the alkoxides which were maintained at 45°C. The reaction mixture was stirred overnight at 40°C and copolymer was precipitated by the addition of 4 liters of benzene and was washed with 6 liters of water. Upon evaporation of organic solvents, a yellow oil (681 g.) was obtained. The white elastomer was dissolved in 4 liters of the azeotropic mixture of  $CCl_2FCClF_2$  with acetone, and the solution was washed with water until the aqueous layer was free of chloride ion (negative  $AgNO_3$  test). The water layer was removed and the copolymer was precipitated by addition of benzene. The procedure was repeated a second time because the copolymer was swollen by the water and efficient removal of salts was impeded. Little oil (5 g.) was obtained upon evaporation of the solvents. Characterization of the copolymer (500 g.) is given in Table I.

TABLE I

Characterization of Large Scale Preparation  
of the Poly(fluoroalkoxyphosphazenes)

Composition	Sample Number	$[\eta]$ dl./g. at 28°C in Acetone	% Cl	Yield Polymer grams	Yield Oil grams	Composition by NMR (mole %)
$[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$	1752-14	0.83 <sup>a</sup>	0.6	1058	525	51.6 C <sub>2</sub> / 48.4 C <sub>4</sub>
$[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$	1752-16	3.1	0.3	546	686	52.3 C <sub>2</sub> / 37.7 C <sub>5</sub>
$[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$	1716-47G	2.2	<0.1	700	517	47.7 C <sub>3</sub> / 52.3 C <sub>7</sub>

<sup>a</sup>  $F[CF(CF_3)CF_2O]_2CHFCF_3$

<sup>b</sup>  $C_2 = CF_3CH_2O$ ,  $C_3 = HCF_2CF_2CH_2O$ ,  $C_4 = C_3F_7CH_2O$ ,  $C_5 = HCF_2C_3F_6CH_2O$ ,  $C_7 = HCF_2C_5F_{10}CH_2O$

<sup>c</sup> F<sup>19</sup>

<sup>d</sup> H<sup>1</sup>

### 2.3 Preparation of $[(\text{HCF}_2\text{CF}_2\text{CH}_2\text{O})_2\text{PN}-(\text{HCF}_2\text{C}_5\text{F}_{10}\text{CH}_2\text{O})_2\text{PN}]_n$

Distilled hexachlorophosphazene (1350 g.) was polymerized in an evacuated glass bomb ( $10^{-6}$  mm.) at  $270^\circ\text{C}$  for 3 hours and at  $250^\circ\text{C}$  for 109 hours. The  $[\text{Cl}_2\text{PN}]_n$  polymer (520 g., 38.5% conversion) was divided and a portion of the polymer (300 g., 2.6 moles) was dissolved in 2.7 liters of dry benzene. Sodium (131 g., 5.7 moles) was placed in 3 liters of dry tetrahydrofuran which was cooled in a  $0^\circ$  bath. Distilled  $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$  alcohol (410 g., 3.1 moles) was added to the sodium over a period of 3 hours followed by distilled  $\text{HCF}_2\text{C}_5\text{F}_{10}\text{CH}_2\text{OH}$  alcohol (1030 g., 3.1 moles) again in 3 hours. The mixture was stirred overnight at room temperature, but a considerable amount of sodium remained and the solution was a light brown color. Additional alcohols (5% by weight of each) were added and the mixture was heated to  $50^\circ\text{C}$  for 6 hours and stirred overnight at  $35^\circ\text{C}$  to completely react all the sodium. The  $[\text{Cl}_2\text{PN}]_n$  polymer solution was added to the alkoxides at  $25-40^\circ\text{C}$  over a period of 5 hours. A thick, white soupy mixture was obtained and was stirred overnight. Copolymer was precipitated as fine white particles by the addition of 7 liters of benzene and washed with 5 liters of water. An oil fraction (446 g.) was obtained upon evaporation of solvents. The cream colored elastomer was purified as described in Section 2.2 except only a single purification was employed (no emulsification difficulty). Evaporation of these solvents gave an additional 70 g. of oil. Characterization of the copolymer (700 g.) is given in Table I.

### 2.4 Nuclear Magnetic Resonance (NMR) Data for the Poly(fluoroalkoxyphosphazenes)\*

The proton ( $\text{H}^1$ ) NMR of  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ , which consisted of an unequivalent triplet at  $\sim 270$  Hz downfield from tetramethylsilane (TMS) due to the overlap of the two  $-\text{CH}_2\text{O}-$  groups, was difficult to interpret. The fluorine ( $\text{F}^{19}$ ) NMR on the other hand could be interpreted and is summarized in Table II.

\* All spectra were obtained at 60 Hz.

TABLE II

$F^{19}$  NMR (Hz) of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$   
Upfield from  $CFCl_3$

$(CF_3CH_2O-)$ $CF_3$	$(CF_3CF_2CF_2CH_2O-)$				$CCl_2FCClF_2/$ Acetone Azeotrope	
	$CF_3$	$CF_2$ in $CF_3CF_2-$	$CF_2$ in $CF_2CH_2O-$		$CF_2Cl$	$CFCl_2$
4304 triplet	4625 triplet	7223 singlet	6880 broad singlet		3864 doublet	4075 triplet

Integration of the two sets of triplets of  $CF_3-$  indicated a composition of 51.6( $CF_3CH_2O$ ):48.4( $C_3F_7CH_2O$ ).

The  $H^1$  NMR of the copolymer of  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  in the azeotrope of  $CCl_2FCClF_2$  with acetone is summarized in Table III. Interpretation was possible in this case because of the long range coupling which takes place between the fluorine atoms and the terminal hydrogen (Ref. 5). This coupling gives three triplets which specify the contribution of the  $HCF_2C_3F_6CH_2O$  group to the unequivalent triplet of  $-CH_2O-$ . By difference the contribution of  $CF_3CH_2O-$  to the  $-CH_2O-$  unequivalent triplet can be calculated.

TABLE III

$H^1$  NMR (Hz) for Copolymer of  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$  Downfield from TMS

$(CF_3CH_2O-)$ $(HCF_2C_3F_6CH_2O-)$ $-CH_2O-$	$(HCF_2C_3F_6CH_2O-)$ Coupled $HCF_2$			$CCl_2FCClF_2/$ Acetone Azeotrope
270 unequivalent triplet	323 triplet	374 triplet	426 triplet	121 singlet

Integration of the three sets of triplets and by difference from the total  $-CH_2O-$  peak, a composition of 62.3( $CF_2CH_2O$ ):37.7( $HCF_2C_3F_6CH_2O$ ) was indicated.

With a few added complications the  $H^1$  NMR for the  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$  was interpreted. The data are shown in Table IV.

TABLE IV

$H^1$  NMR (Hz) for  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$   
Downfield from TMS\*

$(HCF_2CF_2CH_2O-)$ $(HCF_2C_5F_{10}CH_2O-)$ -CH <sub>2</sub> O-	$(HCF_2CF_2CH_2O-)$ Coupled HCF <sub>2</sub> -			$(HCF_2C_5F_{10}CH_2O-)$ Coupled HCF <sub>2</sub> -		
270 unequivalent triplet	307 triplet	360 triplet	412 triplet	326 triplet	377 triplet	429 triplet

\* In the azeotrope of  $CCl_2FCClF_2$ /acetone which gave a singlet at 120 Hz.

In each of the three sets of triplets the lower field triplet was assigned to the terminal proton of the  $HCF_2C_5F_{10}CH_2O-$  substituent on the basis of greater numbers of electron withdrawing fluorine atoms in this substituent which should give the larger deshielding on the terminal proton and on the basis of NMR data for another compound, namely  $[(CF_3CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$ . Integration indicated a ratio of 47.7( $HCF_2CF_2CH_2O$ ):52.3( $HCF_2C_5F_{10}CH_2O$ ) but due to the close proximity and size of the triplets the accuracy of this ratio is less certain than the preceding two copolymers.



### 3.0 PROCESS STUDIES

#### 3.1 Investigation of Reproducibility during the Derivatization of $[\text{Cl}_2\text{PN}]_n$ Polymer

The  $[\text{Cl}_2\text{PN}]_n$  polymer (12.0 g., 0.10 mole) was dissolved in 400 ml. of dry benzene, and the solution was divided into two equal portions. Trifluoroethanol (12.5 g., 0.13 mole) and  $\text{C}_3\text{F}_7\text{CH}_2\text{OH}$  (24.9 g., 0.13 mole) were added to sodium (5.2 g., 0.23 mole) in 400 ml. of dry tetrahydrofuran. The solution of the fluoroalkoxides also was divided into two equal portions. The  $[\text{Cl}_2\text{PN}]_n$  polymer solutions were added to the solutions of the fluoroalkoxides at reflux. The addition times were 3/4 of an hour, and the reaction mixtures were refluxed overnight. Each mixture was treated with the same amount of dilute HCl and the copolymers were each dissolved in the azeotropic mixture of  $\text{CCl}_2\text{FCClF}_2$  and acetone. After all the chloride ion was removed with water, the copolymer solutions were evaporated under vacuum to give white elastomeric products. Properties and yields are listed in Table V. All results appear to agree within experimental error.

TABLE V

Reproducibility of  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$   
Copolymer Preparation

	1699-15-1	1699-15-2
Copolymer yield (%)	79.3	79.8
$[\eta]$ (dl./g.) (a)	0.95	1.1
Chlorine analysis (%)	< 0.1	< 0.1
Composition by $\text{F}^{19}$ NMR (mole % $\text{CF}_3\text{CH}_2\text{O}/\text{C}_3\text{F}_7\text{CH}_2\text{O}$ )	52.9/47.1 (b)	54.4/45.6 (b)

(a)  $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CHFCF}_3$  at  $28^\circ\text{C}$

(b) A rerun gave 54.4/45.6 and 53.6/46.4, respectively.

### 3.2 Effect of Acid and Neutral Water Treatment of the Derivatized $[\text{Cl}_2\text{PN}]_n$ Polymer

Two separate but identical reactions were conducted as described in Section 3.1. However, one reaction mixture was hydrolyzed with dilute acid (10% HCl) while the other mixture was treated only with water. The copolymers were dissolved in the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  and acetone, washed with water, and precipitated by addition to a 10-fold excess of benzene. The copolymers from the unacidified mixture always gave a much more voluminous precipitation than obtained with the acidified copolymers. Table VI summarizes the data collected in two experiments. The high chlorine content of the unacidified samples is unexplained.

TABLE VI

Study of Effect of pH during Hydrolysis  
of  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$

Experiment Number	Sample Number	Yield of Polymer (%)	$[\eta]$ (a) (dl./g.)	Chlorine Analysis (%)	Composition by $\text{F}^{19}$ NMR $\text{CF}_3\text{CH}_2\text{O}/\text{C}_3\text{F}_7\text{CH}_2\text{O}$ (mole %)
1	1699-19B acidified	68	0.75	< 0.1	52.6/47.3
	1699-19-2 unacidified	76	1.4	0.7	52.5/47.5
2	1716-34A acidified	72	0.40	0.2	51.8/48.2
	1716-34B unacidified	68	1.8	0.6	52.1/47.9

(a)  $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CHFCF}_3$  at  $28^\circ\text{C}$

In view of the large differences in intrinsic viscosities of the copolymers which were hydrolyzed with and without dilute acid, further studies were conducted. The effect of treatment with acid on the isolated and purified copolymer from the unacidified hydrolysis was investigated.

Sample 1716-34B (2 g.) was broken into small pieces, slurried with 20 ml. of 10% HCl overnight at room temperature and was washed free of acid with water before being dried under vacuum. There was no visual change in the product and the intrinsic viscosity was 1.3 dl./g. Sample 1716-34B (2 g.) was dissolved in 30 ml. of the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  and acetone and stirred with 20 ml. of 10% HCl for 2 hours. The acid was decanted and the polymer was obtained by evaporation of the solvent. The product had an intrinsic viscosity of 1.6 dl./g.

### 3.3 Investigations into New Purification Procedures

Distilled hexachlorophosphazene (800 g.) was polymerized for 63 hours at  $270^\circ\text{C}$  and 15 hours at  $250^\circ\text{C}$ . The  $[\text{Cl}_2\text{PN}]_n$  polymer (624 g., 5.4 moles) was dissolved in 2.8 liters of dry benzene. Sodium (259 g., 11.3 moles) in 4.5 liters of dry tetrahydrofuran was reacted with  $\text{CF}_3\text{CH}_2\text{OH}$  (621 g., 6.2 moles) at reflux. After addition was complete, reflux was continued for 2 hours and the mixture was cooled to  $35^\circ\text{C}$ . Then,  $\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{OH}$  (1441 g., 6.2 moles) was added at  $35\text{--}40^\circ\text{C}$ . The polymer was added dropwise to the reaction mixture which was maintained at  $35\text{--}40^\circ\text{C}$ . The soupy mixture was heated at  $35^\circ\text{C}$  for 16 hours and stirred over the weekend at room temperature. Benzene (8 liters) was added to precipitate the copolymer. The solvents which were decanted were evaporated to give 760 g. of oil. The copolymer was treated with 10 liters of water twice whereupon some coagulation occurred. The wet solid was divided into three unequal portions and purified by several different wash techniques in order to evaluate their effect on the copolymer and on the time required for purification.

The first portion (A) was dissolved in the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  and acetone, washed extensively with water and precipitated into benzene. An intrinsic viscosity of 2.2 dl./g. at  $28^\circ\text{C}$  and a chlorine analysis of 0.06% were obtained.

The second portion (B) and water were placed in a high speed blender and agitated for one minute. Water was decanted, fresh water was added and the procedure was repeated again and again until the water appeared chloride free. An intrinsic viscosity of 2.3 dl./g. at  $28^\circ\text{C}$  and 0.16% chlorine content were found.

The third portion (C) was masticated in the presence of water with a mortar and pestle over a period of 10 days until

the water showed an absence of chloride ion. An intrinsic viscosity of 2.2 dl./g. at 28°C and a chlorine analysis of 0.09% were found.

A second similar synthesis which employed different methods of purification was carried out. The differences in synthetic procedure were the use of 25% excess alcohol and 15% excess sodium on the basis of polymer, which was prepared at 270°C for 4 hours. Also, the addition of  $\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{OH}$  was conducted at 25°C without overnight heating and the reaction mixture was purified after 16 hours at 35°C. The soupy reaction mixture was divided into three unequal portions which were purified separately.

One portion (D) was treated with isopropanol and benzene was added until all the polymer had precipitated. Solvents were decanted and the solid was washed twice with isopropanol. Salts were extracted from the sample with water in the high speed blender as described above. An intrinsic viscosity of 4.2 dl./g. at 28°C and 0.08% chlorine were found.

The second portion (E) was treated with benzene until the polymer precipitated, and the solid was washed twice with benzene. This sample was blended with water as above. An intrinsic viscosity of 3.3 dl./g. at 28°C and 0.04% chlorine were found.

The third portion (F) was precipitated with benzene and the solid was washed twice with benzene. The material was dissolved in the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  with acetone and washed with water until the aqueous layer was chloride free. An intrinsic viscosity of 5.5 dl./g. at 28°C and 0.21% chlorine were found. Later, a portion of this material was slurried in water and blended. The intrinsic viscosity of the resultant material (portion F<sup>1</sup>) was found to be 5.8 dl./g. at 28°C.

All experiments described above represent single attempts and firm judgements should not be made until these results have been verified. Interestingly, the high speed blender does not appear to affect the molecular weight of the copolymers (compare portions B and C with A and F with F<sup>1</sup>) as judged by intrinsic viscosities. In the second series of experiments, no explanation is offered for the deleterious effect on molecular weight of the benzene precipitation (portion E) versus the isopropanol wash followed by a benzene precipitation (portion D). However, more unremoved alkoxides and fluoro-alcohols would be present in the copolymer from portion E than the one from portion D.

3.4 Attempted Preparation and Characterization of Copolymers of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  with Substituent Ratios of 3:1 and 1:3

The  $[Cl_2PN]_n$  polymer (12.9 g., 0.11 mole) was dissolved in 360 ml. of dry benzene, and the polymer solution was divided into two equal portions. One portion was added to an alkoxide solution at reflux which was prepared from sodium (2.8 g., 0.12 mole),  $CF_3CH_2OH$  (10.0 g., 0.10 mole) and  $C_3F_7CH_2OH$  (6.7 g., 0.03 mole), in 190 ml. of tetrahydrofuran. The reaction mixture was refluxed overnight and dilute HCl (25 ml., 10%) was added to the mixture at room temperature. The copolymer was purified in the normal fashion and a weak, colorless gum was isolated by addition of the polymer solution to benzene. The other portion of the  $[Cl_2PN]_n$  polymer solution was added to an alkoxide solution at reflux prepared from sodium (2.8 g., 0.12 mole),  $CF_3CH_2OH$  (3.3 g., 0.03 mole) and  $C_3F_7CH_2OH$  (20.0 g., 0.10 mole) in 200 ml. of tetrahydrofuran. The copolymer which was a soft, fibrous plastic was isolated as described above. The data obtained for these two copolymers (1716-05, 1716-03) are given in Table VII.

In an effort to determine if the presence of the chlorophosphazene cyclic species during derivatization influenced copolymer composition, another experiment was conducted. Two portions of the same  $[Cl_2PN]_n$  polymer were derivatized with identical alkoxides, but in one reaction the purified poly(dichlorophosphazene) was used while in the other reaction crude material was employed. Yields of the copolymer and oils and the total yield in these companion experiments were sufficiently diverse to make interpretation of this experiment difficult. The results are reported as 1752-34A and 1752-34B in Table VII.

A pair of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymers of 3:1 and 1:3 composition were prepared and described (Ref. 4) previously. They were prepared from different batches of poly(dichlorophosphazene) both of which had not been purified before derivatization. The data for these copolymers are summarized in Table VII. Also included in the Table are individual preparations of several other compositions of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  which have been examined.

TABLE VII

Characterization of Attempted Preparations of  
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  Copolymers of Various Compositions

Cyclics Present	Sample Number <sup>(a)</sup>	$[\eta]$ <sup>(b)</sup> (dl./g.)	Chlorine Analysis (%)	CF <sub>3</sub> CH <sub>2</sub> O/C <sub>3</sub> F <sub>7</sub> CH <sub>2</sub> O Composition (mole %)	
				Attempted	Found <sup>(c)</sup>
Yes	{ 1534-02A	0.80	< 0.1	80.0/20.0	84.3/15.8
Yes	{ 1534-05A	0.72	< 0.1	75.0/25.0	76.6/23.4
No	{ 1716-05	0.03	< 0.1	75.0/25.0	81.5/18.5
No	{ 1716-03	1.1	0.7	25.0/75.0	28.6/71.3
Yes	1556-22	2.9	< 0.1	25.0/75.0	21.3/78.7
Yes	1632-04C	1.7	< 0.1	66.7/33.3	70.8/29.2
Yes	1593-17-8	1.6	< 0.1	60.0/40.0	53.2/46.8
No	{ 1752-34B	0.34	0.4	50.0/50.0	53.3/46.7
Yes	{ 1752-34A	0.31	0.1	50.0/50.0	53.5/46.5

(a) Symbol { indicates identical  $[Cl_2PN]_n$  used in preparations

(b)  $F[CF(CF_3)CF_2O]_2CHFCF_3$  at 28°C

(c)  $F^{19}NMR$

#### 4.0 EXPLORATORY STUDIES OF POLY(FLUOROALKOXYPHOSHAZENES)

##### 4.1 Attempted Preparation and Characterization of $[\{(CF_3)_2CHO\}_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$

Since an earlier attempt to prepare  $[\{(CF_3)_2CHO\}_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$  was unsuccessful (Ref. 6), the procedure was altered and another synthesis was carried out. The  $[Cl_2PN]_n$  (5.8 g., 0.050 mole) was dissolved in 500 ml. of dry tetrahydrofuran. Sodium (1.0 g., 0.045 mole) and  $HCF_2C_5F_{10}CH_2OH$  (16.6 g., 0.050 mole) were reacted in 100 ml. of dry tetrahydrofuran at 23°C. This alkoxide was added rapidly to the stirred polymer solution and the reaction mixture progressed from a gelatinous stage to a uniform fluid mixture (3 hours). This mixture was cooled to 0°C, a solution of sodium hexafluoroisopropoxide at 0°C was added rapidly and one hour later the reaction mixture was allowed to warm to room temperature. The latter alkoxide was prepared at 0°C from sodium (1.2 g., 0.050 mole), hexafluoroisopropanol (11.8 g., 0.070 mole) and 100 ml. of dry tetrahydrofuran. The following day additional alkoxide was prepared in tetrahydrofuran (100 ml.) from sodium (0.4 g., 0.015 mole) and  $HCF_2C_5F_{10}CH_2OH$  (6.6 g., 0.020 mole). This alkoxide solution was added dropwise to the main reaction mixture which was heated to 62°C. The temperature was maintained for 5 hours before solvents were evaporated and the sample was purified. The material was dissolved in the azeotrope of  $CCl_2FCClF_2$  and acetone, was washed exhaustively with water, and benzene was added to precipitate the copolymer. The material was found to have an intrinsic viscosity of 0.78 dl./g. in acetone at 28°C and 0.72% chlorine. Proton NMR showed a ratio of 57.5  $[(CF_3)_2CHO]:42.5(HCF_2C_5F_{10}CH_2O)$ .

##### 4.2 Preparation and Characterization of $[(HCF_2C_3F_6CH_2O)_2PN]_n$

Hexachlorophosphazene (50.0 g., 0.43 mole) was polymerized at 270°C for 3 hours. The contents of the polymerization tube were dissolved in 500 ml. benzene and added to the alkoxide solution at 25°C. Sodium (22.8 g., 1.0 mole),  $HCF_2C_3F_6CH_2OH$  (250.0 g., 1.1 moles), 600 ml. of tetrahydrofuran and a temperature of 0°C were employed in the alkoxide preparation. After addition was complete, the soupy reaction mixture was allowed to warm to room temperature and stirred for 2-1/2 days and was divided into two unequal portions. One portion was refluxed for 24 hours before purification, while the other portion was purified immediately. Both samples were treated with 1.5 liters of benzene to precipitate the polymer, dissolved in the azeotrope of  $CCl_2FCClF_2$  and acetone, and washed

exhaustively with water until no chloride ion was detected. Both polymers were precipitated by addition to benzene. Characterization of these white, weak, fibrous homopolymers is given in Table VIII. Both homopolymers were soluble in acetone, tetrahydrofuran, ethanol and in the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  and acetone. They were insoluble in benzene, heptane and strong mineral acids and bases. Apparently, overnight reflux was deleterious to the homopolymer since the intrinsic viscosity was halved.

TABLE VIII

Characterization of  $[(\text{HCF}_2\text{C}_3\text{F}_6\text{CH}_2\text{O})_2\text{PN}]_n$

Sample No.	$[\eta]$ dl./g. Acetone	Analysis % (a)				Yield Polymer		Yield Oil	
		C	H	N	Cl	grams	%	grams	%
1829-04C Not refluxed	4.9	23.7	1.2	2.9	<0.1	4.7	2.2	79.0	36.1
1829-04-3 Refluxed	2.4	23.6	1.1	2.8	<0.1	7.6	3.5	82.9	37.8

(a)

Calculated values: C, 23.7; H, 1.2; N, 2.8; Cl, 0.0.

#### 4.3 Preparation of $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ Rich in the $\text{C}_3\text{F}_7\text{CH}_2\text{O}$ Substituent

A solution of  $[\text{Cl}_2\text{PN}]_n$  (14.0 g., 0.121 mole) in 75 ml. of benzene was added over 1/2 hour to a solution (60°C) of fluoroalkoxides which was prepared from trifluoroethanol (3.4 g., 0.032 mole), heptafluorobutanol (44.6 g., 0.223 mole), and sodium (5.9 g., 0.255 mole) in 150 ml. of tetrahydrofuran. The mixture was heated 18 hours at 50-60°C, cooled and allowed to settle and the clear liquor decanted and discarded. The solid was pressed dry, dissolved in 1200 ml. of the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  and acetone and washed with water. Polymer was precipitated by addition of 1 liter of benzene. A white fluffy solid (62% yield) which was insoluble in benzene, acetone, chloroform and tetrahydrofuran but was soluble in the  $\text{CCl}_2\text{FCClF}_2$ /acetone azeotrope was obtained. In contrast,  $[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$  swelled but did not dissolve [0.5% (w/w)] in



the  $\text{CCl}_2\text{FCClF}_2$ /acetone azeotrope. The intrinsic viscosity of copolymer in  $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CHF}_2\text{CF}_3$  at  $28^\circ\text{C}$  was 0.93 dl./g. The  $\text{F}^{19}$  NMR indicated the ratio of  $\text{C}_3\text{F}_7\text{CH}_2\text{O}:\text{CF}_3\text{CH}_2\text{O}$  was 6.4:1. Films were prepared from a 3% solution in the azeotrope of  $\text{CCl}_2\text{FCClF}_2$  and acetone by evaporation at room temperature. The films were very flexible but weak. Anal. Calcd: Cl, 0.0. Found: Cl, 0.03.

## 5.0 COMPOUNDING STUDIES

A brief compounding study of the  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ ,  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$ , and  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$  copolymers was initiated. Peroxide cures which had been outlined previously (Ref. 2) were attempted with these poly(fluoroalkoxyphosphazenes). Primary ingredients in the compound formulations were dicumyl peroxide, fumed silica, magnesium oxide, and copolymer. Table IX presents the physical properties determined for representative compositions which were cured at 356°F for one hour.

TABLE IX

### Compounding of Poly(fluoroalkoxyphosphazene) Copolymers

	$[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$	$[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$	$[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$
	1670-26	1778-13	1778-43
Polymer	100 parts	100 parts	100 parts
Silica	14	30	35
Dicumyl peroxide	2	3	3
Magnesium oxide	6	10	6
Tensile strength (p.s.i.)	1100	1080	1490
Elongation (%)	280	200	150
Hardness (Shore A)	59	82	73

Additional studies should increase these values significantly.

A single fluoroelastomer-type cure was attempted with  $[(\text{HCF}_2\text{CF}_2\text{CH}_2\text{O})_2\text{PN}-(\text{HCF}_2\text{C}_5\text{F}_{10}\text{CH}_2\text{O})_2\text{PN}]_n$ , but was unsuccessful. The recipe was:

Copolymer	100 parts
MgO	15
Carbon black MT	20
Diak No. 3	3
Cure conditions	30 minutes at 280°F, post cure 24 hours, 400°F

A partial cure was obtained but during post cure at 400°F the material depolymerized. Other recipes which have been successful in fluoroelastomer systems should be investigated.

## 6.0 DISCUSSION

This contract has been concerned with three separate tasks: (1) large scale synthesis of the poly(fluoroalkoxyphosphazene) copolymers which are most likely to meet Army needs for extreme service rubbers, (2) process studies to improve synthesis techniques and product properties, and (3) exploratory synthesis. In addition, the availability of poly(fluoroalkoxyphosphazenes) in quantity made possible some preliminary compounding studies.

Three copolymers were prepared in approximately two pound quantities. These copolymers,  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ ,  $[(CF_3CH_2O)_2PN-(HCF_2C_3F_7CH_2O)_2PN]_n$ , and  $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$ , were known (Ref. 4) to have outstanding low temperature fuel-resistance properties. Scale-up was accomplished with little difficulty but the solution purification of the derivatized copolymers became quite burdensome for such large preparations. Preliminary studies of purification in the solid state are encouraging. Characterization of the three copolymers indicated that these elastomers were equivalent to the same materials prepared on a smaller scale. The only disappointment was the higher than average chlorine content found for the  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymer, but this is almost certainly not related to the increased scale of synthesis. In conclusion, given suitable equipment, little problem is envisioned in further scale-up of the preparation of these materials.

Since an adequate supply of these three copolymers was available, curing and compounding studies were performed. These attempts quickly surpassed results achieved previously (Ref. 2) largely because the difficulties of compounding on the micro-scale could be avoided. Certainly much work remains to be done, but preliminary results are quite encouraging. With this modest effort tensile strengths of 1080-1490 p.s.i. and elongations of 280-150% were obtained for these copolymers. Future progress above these values is anticipated.

Several process studies were undertaken. A determination of the ability to reproduce the preparation of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  was carried out. Identical poly(dichlorophosphazene) was reacted separately with two aliquots of a stock solution of  $CF_3CH_2ONa$  and  $C_3F_7CH_2ONa$ . The elastic products were examined and are thought to be essentially identical.

The effect of pH during hydrolysis of the  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  reaction mixture also was studied. Reactions

were conducted as described above in the reproducibility experiment except the separate reaction mixtures were hydrolyzed under different conditions. Several startling and as yet unexplained results were observed. Acidified reaction mixtures seem to lead to copolymers with much lower intrinsic viscosities and chlorine contents than unacidified mixtures. In additional experiments, the copolymer from the unacidified mixture was isolated and purified and treated with dilute acid both in the solid state and in solution. There was little effect on intrinsic viscosity. Further studies are planned.

Various types of purification of  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymers in the solid state were investigated. These studies were desirable because as the size of the copolymer preparation was increased, solution purification became less and less attractive. The main difficulties were solution of the copolymer, efficient mixing of the resultant slurry and the long drying times of the precipitated copolymer. Apparently, short but repeated agitation in a high speed blender will rapidly remove sodium chloride and render the copolymers in a form which is easily dried. Additional work will be needed to ascertain optimum isolation procedures before blending and also to determine the effect of blending on properties (particularly on molecular weight).

The relative ratios of substituents in several  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymers were studied with  $F^{19}$  NMR. Variations in composition would be likely to give copolymers with different physical properties. These investigations were conducted to determine whether the presence of cyclic phosphazenes during derivatization influenced the composition of the copolymer, and whether one substituent group reacted faster than the other even in the absence of cyclics. A pattern to the results has not become apparent. Some further studies should be conducted before this line of investigation is abandoned.

Several exploratory syntheses were carried out. Greatest emphasis (see also Ref. 6) was placed on the preparation of a homopolymer and several copolymers which contained the hexafluoroisopropoxide  $[(CF_3)_2CHO]$  moiety. Preparation of tetrahydrofuran solutions of sodium hexafluoroisopropoxide proved to be considerably more difficult than preparation of solutions of the sodium salts of unbranched fluoroalcohols. Successful preparations required low temperatures and short storage times. However, even with these precautions, completely substituted poly(phosphazenes) were not obtained. Incomplete substitution may be related to the lowered basicity of sodium

hexafluoroisopropoxide and/or steric problems as compared to the salts of the unbranched fluoroalcohols.

The  $[(C_3F_7CH_2O)_2PN]_n$  homopolymer has shown promise as a chemical resistant coating. However, it lacked practicality since it was soluble only in exotic solvents such as  $CF_3CF_2CF_2OCHF_2CF_3$ . A  $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$  copolymer was prepared which had a substituent ratio of 6.4  $(C_3F_7CH_2O):1(CF_3CH_2O)$  and was found to be soluble in the azeotrope of  $CCl_2FCClF_2$  and acetone. This new composition (and close variations) may offer more practical, chemical-resistant coatings.

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